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PYROMETALLURGICAL RECOVERY OF NICKEL AND VANADIUM FROM ATHABASCAN TAR SANDS FLY ASH

BY

G.V. Sirianni and G.E. Viens

Metals Reduction and Energy Centre

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Mines Branch Investigation Report IR 72-23

PYROMETALLURGICAL RECOVERY OF NICKEL AND VANADIUM FROM ATHABASCAN TAR SANDS FLY ASH

by

G.V. Sirianni* and G.E. Viens**

SUMMARY

Three pyrometallurgical routes for the recovery of marketable nickel and vanadium from the fly ash residue resulting from the extraction of petroleum from the Athabascan tar sands have been investigated.

Sulphide Smelting

In this case the fly ash is smelted with sufficient sulfur in the charge to ensure that most of the nickel and part of the iron will be converted to a matte. The vanadium would be retained in the slag as an oxide from which it could be recovered as ferrovanadium by smelting using silicon or aluminium as the reducing agent. Alternatively to extracting the vanadium from this slag by pyrometallurgical techniques, it could possibly be recovered by leaching.

Selective Reduction of Oxides

In this case, it is necessary to pre-treat the ash to minimize the sulfur content and to control the carbon content. This pre-treatment can consist of a roasting step or a flotation step. The flotation appears to be the most practical. After suitable pre-treatment, the ash is smelted with sufficient carbon in the charge to reduce all the nickel and part of the iron to ferronickel. The vanadium is retained as an oxide in the slag from which it could be recovered by the same techniques outlined for the sulfide case.

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*Research Scientist and **Head, Pyrometallurgy Group, Metals Reduction and Energy Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Total Reduction of Oxides

In this case the ash would require the same pre-treatment as that outlined for the selective reduction route. After pre-treatment, the ash is smelted with sufficient carbon to reduce all the nickel, iron, vanadium, and some silicon. The slag consisting of about 90% of the ash weight after pre-treatment would be discarded. Alternative routes for the separation of nickel and vanadium from this slag are possible which require further investigation. One possibility is the use of hydrometallurgical techniques. Another is to oxidize this metal in a converter and remove the silicon, vanadium, and part of the iron as a slag or fume leaving the nickel as ferronickel which could be marketed. The vanadium-bearing slag or fume could be reduced to produce ferrovanadium or leached for the production of vanadium compounds.

Total reduction of oxides appears to be the most promising route and, in our opinion, it is worth experimentation on a larger scale.

INTRODUCTION

In the Spring of 1968 Mr. A.R. McPherson of Bechtel and Company, Montreal, P.Q. approached the Pyrometallurgical Section to discuss the recovery of nickel and vanadium from the fly ash residue that results from the extraction of petroleum from the Athabascan tar sands. About 150 lb of this fly ash was delivered to the Branch in June of 1968. This sample permitted only four preliminary smelting tests, and no more fly ash was available before June 1971.

EXPERIMENTAL WORK

Pre-Treatment of Ash before Smelting

The chemical analyses of the two samples of fly ash are given in Table 1.

TABLE 1

Chemical Analyses of Ash

Constituent (%)	Shipment	
	1968	1971
Ni	0.54	0.66
V	1.48	1.4
Fe	12.3	4.11
CaO	3.52	2.8
MgO	0.85	1.01
SiO_2	25.1	24.8
Al_2O_3	14.0	14.6
S	7.37	2.16
P	0.05	0.03
C	10.8	39.8
LOI	33.5	42.9

Before either of these materials could be smelted as oxides it was necessary to remove most of the sulfur and to lower their carbon content to the amount required to reduce the nickel and part of the iron to metal. Roasting in air appeared to be an obvious technique for removing both sulfur and carbon. Approximately 1/2 of the 1968 sample was roasted in one experiment and

about 700 lb of the 1971 sample was roasted in two experiments. This roasting operation proved to be a rather difficult chore. Dust losses were severe and a surprisingly high energy input was required to maintain this material at combustion temperature. Undoubtedly equipment could be developed which would be much more efficient than the rotating retort that was available in the laboratory for this work. The need to develop such equipment has been circumvented however by the development of a relatively simple flotation scheme by the Mineral Processing Division of the Mines Branch, which recovers approximately 90% of the nickel and 86% of the vanadium. Details of this work are reported in Mines Branch Investigation Report IR 72-19 entitled "Flotation of Carbon from Great Canadian Oil Sands Fly Ash by A. Stemerowicz and R.W. Bruce. The analysis of the products of the roasting and flotation experiments are shown in Table 2.

TABLE 2

Chemical Analyses of Roasted Ash and Flotation Product

Constituent (%)	1968 Shipment Roasted Product	1971 Shipment		
		Roasted Product		Flotation Product
		Expt 70-2-7	Expt 70-2-15	
Ni	1.05	2.1	1.32	1.1
V	2.25	2.25	2.45	2.02
Fe	15.1	7.82	7.2	6.9
CaO	6.51	5.1	4.7	4.06
MgO	1.33	1.6	1.5	1.67
SiO_2	37.2	42.8	43.9	43
Al_2O_3	21.2	24.5	26.8	25.9
S	0.34	0.36	0.28	0.05
P	0.04			
C	0.08	0.55	0.15	0.21
LOI		1.04	0.73	0.52

Sulphide Smelting, Flowsheet 1

Two smelting experiments were performed in a 60-kVA manually controlled arc furnace with the 1968 sample of ash and eight with the 1971 sample. The charge compositions, analysis of products and recoveries of the most important elements are given in Table 3.

The details of the charge compositions given in this table shows that with the earlier sample it was possible to make matte without altering the sulfur in the ash and that the grade of matte could be altered by eliminating part of the sulfur by roasting. The more recent sample, however, required sulfur additions before matte could be produced. This sulfur was added either as iron sulfide or as gypsum. Any addition of gypsum had to be accompanied by carbon which could be added in the form of "as received" ash. The use of gypsum has the advantage of not increasing the iron content of the products. Charges with relatively low sulfur levels and one with a very high level of sulphur were included in this series. In four of the experiments with the 1971 sample, very little limestone was included in the charge in order to minimize the slag volume. In these experiments, the calculated $CaO + MgO:SiO_2$ ratio in the slag was about 0.2:1 which is a rather acid slag and tends to be viscous. In the other four experiments limestome additions were made to yield slag which had a calculated $CaO + MgO:SiO_2$ ratio of about 1:1.

The data in Table 3 indicates that, although there are some discrepancies, the nickel contents of the matte and slag are controlled by the sulfur content of the charge. The high-sulfur charge in Experiment 25 produced a matte containing only 12 % Ni and a slag containing 0.12 % Ni, whereas the comparatively low sulfur used in Experiment 17 resulted in 40% Ni in the matte and 0.36 % Ni in the slag.

The addition of lime appears to have slightly improved the recovery of nickel in the matte but it had the undesirable effect of diluting the vanadium in the slag and thus increasing the difficulty of recovering vanadium in a subsequent step.

The most significant fact which emerges from these data, however, is that, although slag with a relatively low nickel content was successfully produced in some of these experiments (0.12 in Experiment 25 and 0.18 in Experiment 18), the losses of nickel to the slag are about 15 % or higher. A recent article[1] indicates that commercial operations produce slags containing from about 0.1 to 0.3 % nickel. It is therefore not expected that

TABLE 5

Matte Smelting

Experiment No.	68-5-11	68-5-12	70-2-14	70-2-12	70-2-13	70-2-16	70-2-17	70-2-18	70-2-19	70-2-25
harge (lb)										
1968 ash "as rec'd"	22.5	21.2								
" " roasted		3						3.5	4.2	15
1971 ash "as rec'd"			25*	25*	25*	22.2*	25**	25**	25***	15***
" " roasted										
" " flotation product										
FeS			3	2	1	0.67	1			
Fe_2O_3	2.4									
Stone	9.8	10.3	1	1	1	1	16.1	14.5	14.5	3
Gypsum								5	6	18+
roducts (lb)										
Matte button	0.8	1.55	1.7	1.7	0.45	1.59	0.89	1.12	0.52	1.43
" shot			0.3	0.15	0.15	0.22	0.1	0.17	0.33	0.2
Slag	18.3	18.7	23	22.1	22.6	24.5	27.9	32.8	32.7	31.8
tte Analysis (%)										
Ni	6.78	7.14	17.6	17.1	36.2	28.8	40.2	26.9	23.6	12
V	0.33	0.42	1.26	1.8	0.77	1.55	0.17	0.65	0.41	4.05
Fe	57.9	65	55.3	59.9	47.2	55.7	43.2	54.1	56.5	57.6
S	24.7	23.2	19.2	15.9	12.1	13.1	12.7	17.2	17.7	20.8
ag Analysis (%)										
Ni	0.21	0.11	0.36	0.36	0.55	0.36	0.36	0.18	0.20	0.12
V	1.34	1.63	2.17	2.11	2.37	2.3	1.75	1.73	1.58	1.35
Fe	16.3	8.7	8.6	6.67	7.92	6.4	6.6	3.43	4.04	2.0
S	1.5	1.12	0.23	0.18	0.14	0.08	0.27	0.44	0.49	1.58
covery (%)										
ickel in matte	44.9	75.8	67	60.2	41.3	111.8	120.3	98.3	66.3	75.5
slag	31.7	14.1	15.8	15.2	23.6	18.9	30.3	16.7	21.5	14.3
total	76.6	89.9	82.8	75.4	64.9	130.7	150.6	115	87.8	89.8
anadium in matte	0.8	1.7	4.4	5.9	0.9	5.6	0.3	1.2	0.5	12.9
slag	73.8	80	88.6	82.8	94.7	112.6	80	86	77.9	84.3
total	74.6	81.7	93	88.7	95.6	118.2	80.3	87.2	78.4	97.2
ron in matte	13.4	33	28.6	34.3	10.9	46.8	17.5	35.9	25.2	56.6
slag	86.6	53.3	51.2	45.7	69.1	72.6	75.4	58.1	69.4	38.6
total	100	86.3	79.8	80	80	119.4	92.9	94	94.6	95.2

*Roasted ash from Experiment 70-2-7
" " " " 70-2-15

+ $CaSO_4 . \frac{1}{2}H_2O$, other used was $CaSO_4 . 2H_2O$

values significantly lower than those shown in Table 3 could be obtained from this material. Basically, the problem is that this ash contains more than 75 % of slag-forming ingredients; therefore, even low-nickel slags represent significant losses of nickel. The problem is further complicated if the slag has to be re-smelted to recover vanadium. This nickel, because it is easier than vanadium to reduce will be recovered in significant quantities in the ferrovanadium product.

Ferrovanadium Smelting

Two experiments were performed in which slag from Experiments 18 and 19 were reduced with powdered aluminum to produce ferrovanadium. The data for these experiments are given in Table 4.

These experiments confirmed that the nickel lost to the slag in the matte smelting operation would contaminate the ferrovanadium produced from this slag. These experiments also indicate that it is difficult to reduce all the vanadium from this slag. Even though enough aluminium was added to produce a metal containing over 20 % silicon, the slag still contained about 0.5 % vanadium. Because of the large slag volume, this represents a loss in vanadium of 30 to 40 %. It is believed that this loss was more severe because of the small scale of operation (only 2 lb of metal was produced from about 30 lb of slag). It is expected that a larger operation would give better recoveries particularly, if some form of mixing such as is used at Riddle Oregon[2] for ferronickel production were employed.

Selective Reduction of Oxides, Flowsheet 2

During the preliminary experiments using the 1968 sample the objective was to selectively reduce the nickel and part of the iron to produce a ferronickel. The vanadium would be retained in the slag from which it could be recovered as ferrovanadium by an aluminium or silicon reduction. The results of the two experiments performed in this series are given in Table 5.

From these data it can be seen that a low-grade ferronickel can be made by this route. The grade could be improved by controlled oxidation of the iron by blowing air or oxygen into the molten metal. No attempt was made to reduce these slags to ferrovanadium but results very similar to those obtained from the slags produced during the matte smelting experiments could be expected because the compositions of the vanadium-bearing slag was very similar by both routes.

TABLE 4

Production of Ferrovanadium

Experiment No.	70-2-20	70-2-24
Charge (lb)		
Slag from Expt No.	70-2-18	70-2-19
Weight of Slag	31.75	32.1
Aluminum Powder	2.03	1.5
Stone	3.75	2.8
Product (lb)		
Metal	1.85	1.95
Slag	30.2	35.8
Metal Analysis (%)		
Ni	1.18	1.28
V	13.5	16.2
Fe	52.5	
S		
Si	24.3	20.7
Al	0.33	0.09
C	0.5	0.63
Slag Analysis (%)		
Ni	0.049	0.12
V	0.80	0.46
Fe	0.44	0.66
Recovery (%)		
Nickel in metal	38.6	39.1
slag	26.3	62.5
total	64.9	101.6
Vanadium in metal	45.4	62.7
slag	43.6	31.4
total	89.0	94.1
Iron in metal	89	
slag	11.9	
total	100.9	

TABLE 5

Production of Ferronickel from 1968

Shipment of Ash

Experiment No.	68-5-9	68-5-10
Charge (lb)		
Roasted ash 1968 shipment	15	15
Coke ($-\frac{3}{4} + \frac{1}{4}$")	0.95	1.5
Stone	8.3	8.3
Fluorspar	0.38	0.44
Products (lb)		
metal	0.27	1.30
slag	19.9	21.2
Metal Analysis (%)		
Ni	27.2	10.3
V	0.039	0.16
S	0.13	0.20
C	0.07	0.15
Slag Analysis (%)		
Ni	0.19	0.11
V	1.28	1.39
Fe	8.79	6.02
Recovery (%)		
Nickel in metal	46.1	85.3
slag	23.9	14.7
total	70	100
Vanadium in metal	0.03	0.6
slag	75.4	87.2
total	75.43	87.8

Total Reduction of Oxides, Flowsheet 3

The matte smelting and the selective reduction routes to produce ferronickel had a common defect. The slag:metal or the slag:matte ratio was so high that the nickel loss to the slag remained high even though the nickel content of the slag was as low as could be expected, about 0.2 %. The slags produced by either the matte smelting or the selective reduction of oxide routes contain no more than 2 % vanadium. This results in another unfavourable slag:metal ratio when ferrovanadium is reduced from this material, which makes it difficult to minimize vanadium losses. In an attempt to alleviate this difficulty, the Mineral Processing Division was requested to examine the fly ash to determine if it were possible to separate nickel, iron, and vanadium values from the gangue constituents in addition to carbon separation already accomplished. It was found that, except for carbon, fly ash is composed almost entirely of silicates and that separation by mineral dressing was practically impossible.

In the light of this information, it was decided to attempt a pyrometallurgical separation. Magnetic roasting and metallizing roasting were both attempted without success. It was then decided to attempt to reduce all the metal oxides to the metallic state using carbon as the reductant. In this case, the objective was to recover all the metallic values in a molten metal (about 10 % of the weight) and to produce a relatively clean slag which could be discarded.

Three experiments were performed in this series. In all these experiments the carbon contained in "as received" ash constituted most of the reductant. In one experiment, a small addition of carbon in the form of coke was included in the charge.

The data on these experiments are given in Table 6. The recoveries, particularly of vanadium, were erratic for the relatively low vanadium in the slag particularly in Experiment 26, there should have been a relatively high recovery of this element in the metal, whereas this experiment shows the poorest recovery of vanadium in these three experiments. This may be explained in part, by the large quantity of metallics (1.07 lb) that was recovered by magnetic separation from the slag in the form of shot and by the low recovery of massive metal (0.6 lb) that had separated from the slag in the molten state. The reason the metal did not coalesce and settle from the slag is not completely understood. It has been our experience that this condition is most frequently encountered when a new furnace lining is used and a new one was installed just prior to this experiment. However

TABLE 6

Production of Ni-Fe-V-Si-C Alloy

from 1971 Shipment of Ash

Experiment No.	70-2-8	70-2-21	70-2-26
Charge (lb)			
Ash as rec'd	7.5	7.5	7.5
Ash roasted (Expt 70-2-7)	22.5		
Flotation product		22.5	22.5
Stone	1.0	17.7	16.5
Coke			1.0
Products (lb)			
Metal button	2.22	2.07	0.6
Metal shot	0.75	0.19	1.07
Slag	23.6	36.6	32.7
Metal Analysis (%)			
Ni	14.8	11.9	16.2
V	14.9	11.2	13.2
Fe	56.8	68.8	62.9
S	0.09		
Si	7.77	0.29	3.19
C	3.1	4.24	4.48
Slag Analysis (%)			
Ni	0.46	0.068	0.22
V	0.73	0.87	0.35
Fe	0.88	0.93	0.56
Recovery (%)			
Nickel in metal	84.1	90	90
slag	20.8	6.7	23.3
total	104.9	96.7	113.3
Vanadium in metal	72.5	45	39.6
slag	28.2	57.6	19.8
total	100.7	102.6	59.4
Iron in metal	81.5	83.3	56.5
slag	10	18.3	9.7
total	91.5	101.6	66.2

this series of experiments demonstrated that slags reasonably low in nickel and vanadium can be produced and that metal containing 12 - 16 % Ni, 11 - 15 % V, 60 - 70 % Fe, 3 - 5 % C, and up to 10 % Si can be produced from this fly ash.

The question arises as to what can be done to render this metal marketable. Possibly the most obvious route is to selectively re-oxidize it to get rid of C, collect Si, V and part of the iron into an oxide fume or slag, and leave the Ni and the balance of the iron as a high grade ferronickel. The vanadium would have to be reduced from the slag or fume but, at least, it would be more concentrated than in any of the schemes described earlier in this report.

A two-pound sample of metal was melted in the high-frequency furnace, and oxygen was injected through the surface of the bath; see Table 7. Carbon was burned off and a very small quantity of slag was formed.

The composition of this slag is interesting in that it contains substantial quantities of Fe and V but a relatively small amount of Ni. This nickel value is probably artificially high because metal could have been trapped very easily in this very thin layer of slag.

DISCUSSION

The processes proposed in this report for the extraction of nickel and vanadium are all continuous in nature and should be investigated under steady-state conditions. The batch-scale experiments reported here should all be considered as preliminary.

An example of the type of difficulty that is encountered in investigating a continuous pyrometallurgical process by a batch experiment is evident in Table 3 of this report. The total recovery or accountability of nickel in Experiment 17 is shown as 150 %, an obvious impossibility. The high recovery in this experiment was undoubtedly due to low recoveries in preceding experiments. The build-up material from one experiment to the next not only affects the recovery but, unfortunately, also alters the composition of the products. It is therefore necessary to accept the results of this scale of experimentation as a guide rather than as absolute values and to take into consideration published data, data from other projects, and theoretical considerations when assessing the results of these experiments.

TABLE 7

Oxygen Blowing of Metal Produced in

Experiment 70-2-21

Expt No. 70-2-	Object	Time after Meltdown (min)	Oxygen Charged (l)	Constituent (%)					Remarks
				Ni	V	Fe	Si	C	
23A	Oxygen blowing of metal from Expt 70-2-21	0	15	13.6			0.27		
23B	Continuation of Expt 70-2-23A	0	6.6						
		2	7.6						
		4	5.2						
		5	5.2						
		6	-	12.3	10.5	70.3			Sample taken
		7	4.8						
		8	5.2						
		11		13.4	10.0	71.4			Sample taken
		12	5.7						
		13	4.8	12.8	8.9	73.5			Sample taken
				12.9	9.4	73.9	0.28	0.16	metal after cooling
				2.33	28.5	24.2			Slag on metal after cooling

Analysis of metal produced in 70-2-21

Ni	11.9 %
Fe	68.8
V	11.2
Si	0.28
C	4.24

In our opinion, the selective oxidation of C, Si, V, and part of the Fe from the C-Si-V-Fe-Ni alloy is particularly difficult to perform on a small scale. On a larger scale, the heat sink provided by a large quantity of molten metal would be of great assistance in stabilizing the oxidation reactions.

A number of alternative routes are possible for the recovery of Ni and V that have not been investigated in this program. This is particularly true for treatment of the metal produced when carbon is used as the reductant and essentially all the Ni, V, Fe, and some Si are reduced to a metal (Flowsheet 3). Various techniques for oxidizing this metal could be tried. Unsmelted ash could be used as a source of part of the required oxygen. Air, oxygen enriched air, or pure oxygen could all be tried in either bottom blown or top blown vessels. The operating technique could probably be altered to yield the oxidized fraction as a fume or as a liquid slag. It should be possible to control this oxidation step to yield a very high vanadium product an intermediate product, containing V, Fe and Ni, which might be recycled, and a high-grade ferronickel. Leaching could certainly be investigated as a means of recovering elements from some of these products.

A meaningful investigation of these alternatives, however can only be performed after a substantial supply of the Ni-Fe-V-Si-C alloy is available.

One of the considerations, which in our opinion encourages continued work on this project, is that the ash, after the carbon has been removed by flotation, contains 1.1% nickel, which is about 2/3 of the nickel content of the ore that is being mined for ferronickel production at Riddle, Oregon[2]. The ash appears to have other advantages to offset to some degree this lower nickel content. It would not be necessary to purchase a reducing agent because the carbon in the "as received" ash could be used as the reducing agent. Further, the ash contains a substantial quantity of vanadium which can be recovered as a marketable product.

Recommendations

It is recommended that continuous-process work be performed on this project.

All the routes may deserve more attention, for example, if ferrovanadium containing some nickel can in fact be marketed then the matte smelting route has some promise.

The route, however, which in our opinion has the greatest promise, is the total reduction, by carbon, of oxides to produce an alloy of all the metals. This could be a relatively efficient and not excessively expensive concentration step in that all the values are concentrated in about 10 % of the original weight after the carbon has been removed. We estimate, based on general smelting experience, that about 1000 kWh of electrical energy will be required for each ton of feed.

The selective re-oxidation to produce ferronickel is less well defined by the experiments described in this report but, theoretically it should work. In any case, a substantial supply of the Ni-Fe-V-Si-C alloy produced by this route would be required before the oxidation step could be investigated in detail.

It is suggested that a co-operative project between the owners of this ash or their representative and the Mines Branch be organized to share the cost of a larger-scale investigation.

The objectives of this investigation would be to:

(1) Prove on a pilot plant scale of operation that flotation is a practical means of separating the carbon from the ash. This could probably be done at the Mines Branch.

(2) Agglomerate the carbon-free ash to make a suitable feed for smelting. The Mines Branch is equipped to sinter, pelletize, and briquette, but the rate particularly of pelletizing would be slower than desired. Possibly outside facilities should be examined before finalizing this part of a project.

(3) Electrically smelt the agglomerates to:

    (a) determine the relationship between Si content of the Ni-Fe-V-Si-C alloy and the V losses to slag to optimize the economy of the operation;

    (b) determine the power consumption per unit of charge or product;

    (c) produce a sufficient quantity of metal to continue study of techniques of separating the nickel from the vanadium — the Mines Branch is equipped with a 250-kVA electric smelting furnace that could be available for this work.

(4) Study the feasibility of separating by selective oxidation the vanadium from the nickel in the alloy produced in (3) to produce marketable ferronickel — at the present, the Mines Branch has only limited capability in this area, but this capability is currently being increased and in a few months it may be adequate.

(5) Leach the furnace products containing vanadium (3 and 4 above) — the Branch has considerable capability in this area that could be available.

(6) Study the reduction of ferrovanadium from the oxidation products (4 above) to determine what alloys could be produced — the Mines Branch has considerable capability for this aspect of the study.

CONCLUSIONS

Several routes have been developed for the recovery of most of the nickel and vanadium contained in the fly ash resulting from the extraction of petroleum from Athabascan tar sands. The scheme outlined in Flowsheet 3 appears to be worth experimentation on a larger scale.

REFERENCES

1. G.J. Brittingham, "Nickel Production", Australian Mining, August, 1970.

2. E.E. Coleman and D.N. Vedensky, "Ferro-Nickel Production in Oregon", Journal of Metals, March 1960.

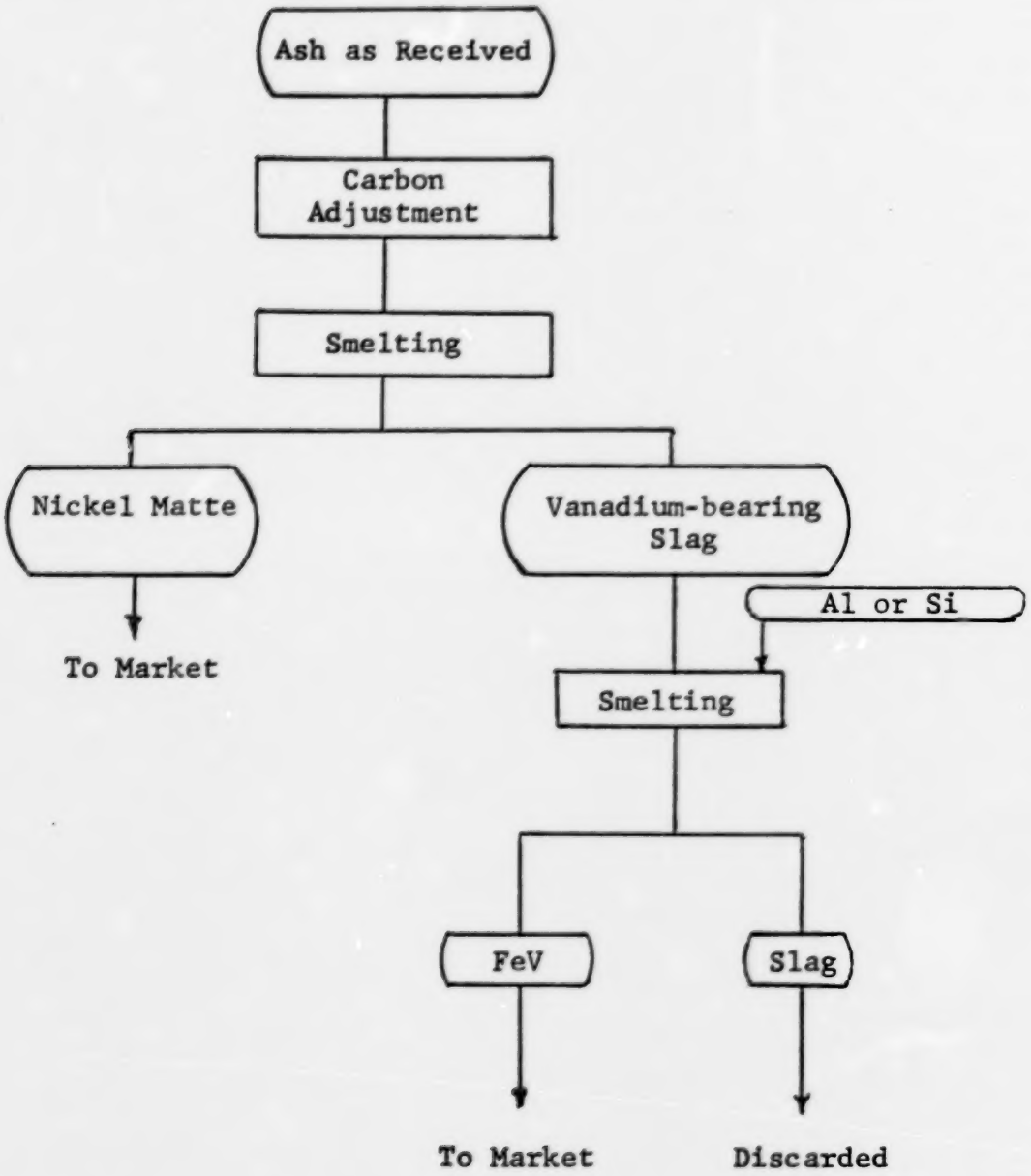

Fig. 1. Flowsheet 1

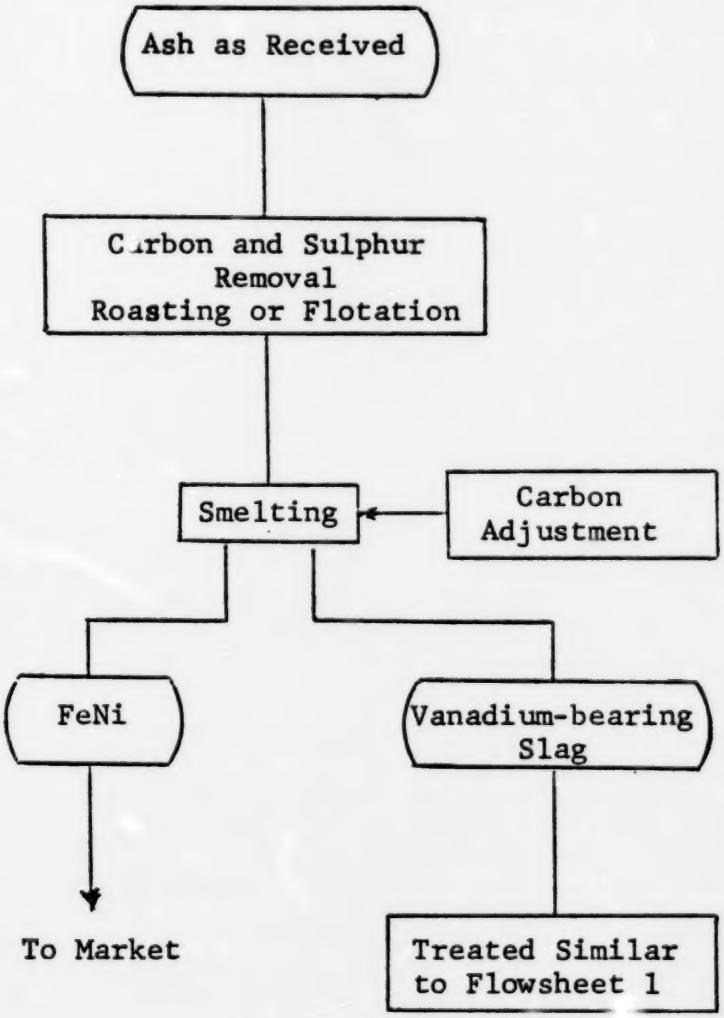

Fig. 2. Flowsheet 2

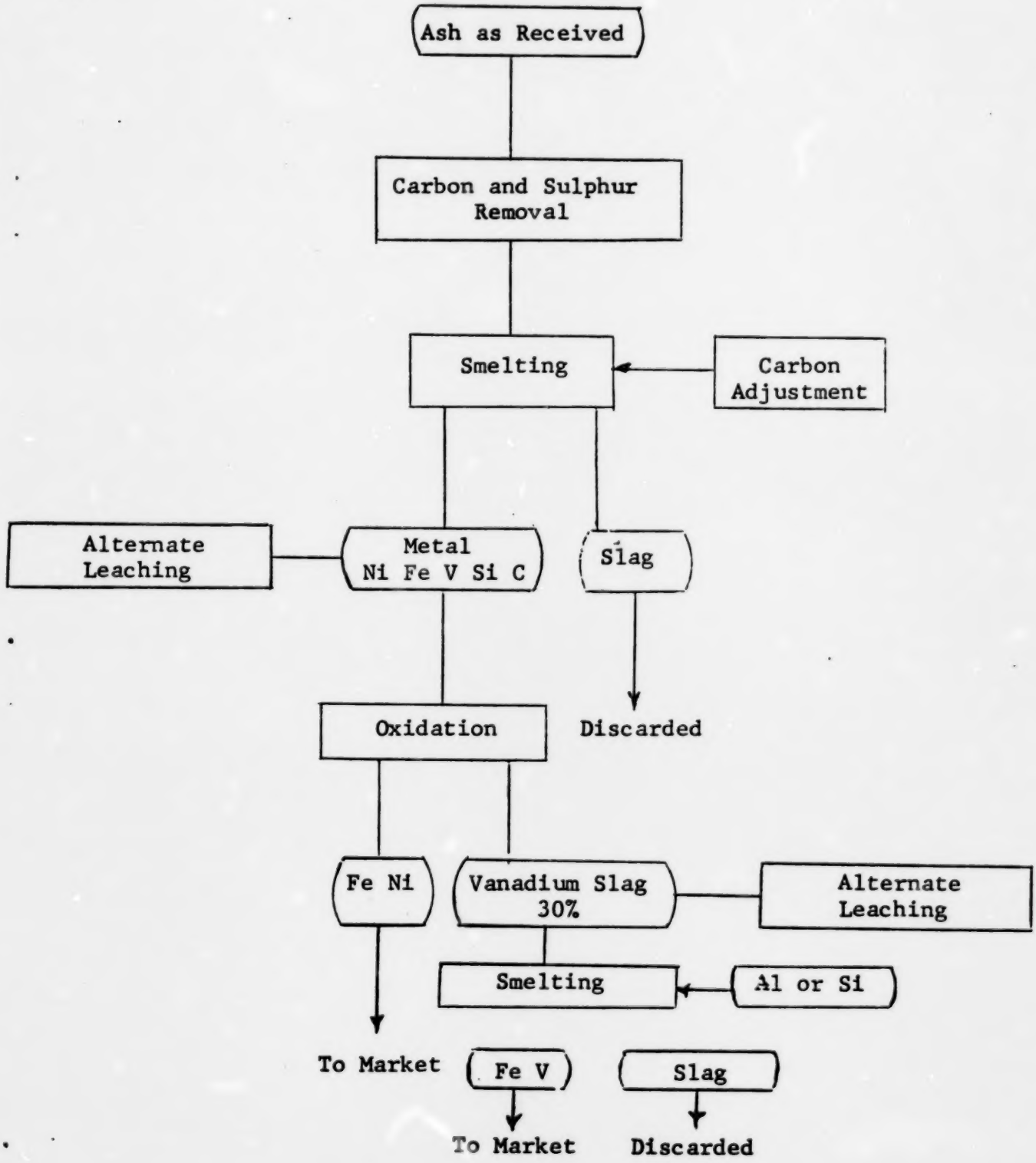

Fig. 3. Flowsheet 3

POOR

QUALITY

ORIGINAL